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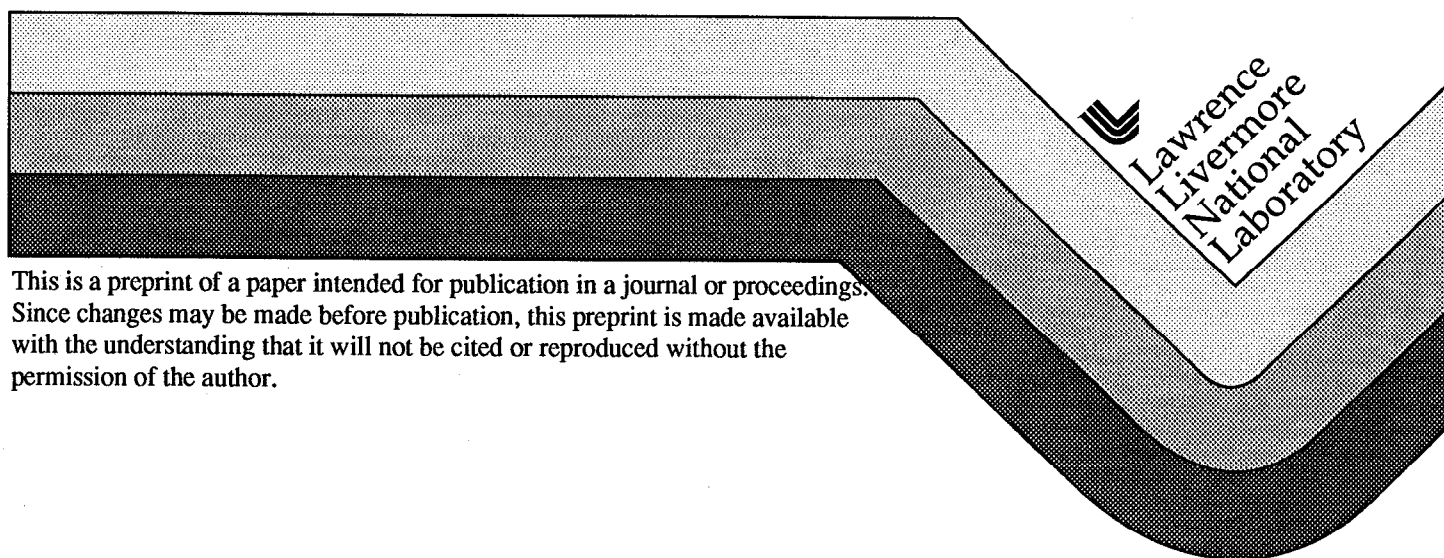
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FIRST PRINCIPLES CALCULATIONS FOR LITHIATED MANGANESE OXIDES

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ABSTRACT

First principles calculations using the local-spin-density-functional theory are presented of densities of electronic states for MnO, $LiMnO_2$ in the monoclinic and orthorhombic structures, cubic $LiMn_2O_4$ spinel, and $\lambda–MnO_2$ (delithiated spinel), all in antiferromagnetic spin configurations. The changes in energy spectra as the Mn oxidation state varies between 2+ and 4+ are illustrated. Preliminary calculations for Co-doped $LiMnO_2$ are presented, and the destabilization of a monoclinic relative to a rhombohedral structure is discussed.

INTRODUCTION

First principles methods, particularly those based on local-density-functional theory (LDFT), are becoming a valuable tool for elucidating the structure and electrochemical properties of candidate cathode materials for Li insertion batteries. LDFT total energy calculations in conjunction with cluster expansions have recently been employed [1,2] to investigate phase stability and Li ordering in the layered oxide Li_xCoO_2, currently used in commercial Li-ion batteries. Three of the present authors have recently performed LDFT calculations to investigate the structure of the two monoclinic phases of the vanadium gamma bronze, $Li_{1+x}V_3O_8$ [3], a material also under consideration as a possible cathode material. A great deal of experimental attention is currently being devoted to lithiated Mn oxides, owing to their practical advantages compared to the Co-based system. Improved theoretical understanding would benefit this effort.

A complication for Mn oxides is the strongly magnetic character of Mn ions. Density functional theory calculations show that spin polarization has a small effect for Li_xCoO_2 (total energy reduction of the order of 0.01 eV/formula unit [1] relative to non-spin polarized calculations), which is most likely also the case for the vanadium γ-bronze [3]. Calculations for monoclinic $LiMnO_2$ [4], however, show an energy reduction of several tenths of an eV per formula unit in spin-polarized treatments. Spin polarization is, therefore, essential to obtain the most realistic description of Mn oxides. In recent work [5], Mishra and Ceder have performed an extensive first-principles study of manganese oxides in several crystal structures at different levels of lithiation both with and without spin polarization. They found that the relative stabilities and structures of the different phases are well described in calculations based on the generalized gradient approximation (GGA) [6], a formulation in which local-spin-density-functional theory is augmented by gradient corrections. For all of the structures on which they made comparisons, antiferromagnetic configurations were favored over ferromagnetic configurations in the calculations based on the GGA.

In this paper, densities of electronic states are presented for several standard Mn oxides in antiferromagnetic configurations with Mn oxidation states between 2 and 4. The results illustrate the electronic structure at various levels of filling of the majority spin e_g band. Preliminary calculations for Co-doped Mn dioxides are also discussed, which are intended to elucidate the recent experimental finding [7] that such doping tends to stabilize the rhombohedral structure relative to the one with monoclinic symmetry.

METHOD

Spin-polarized (LSDFT) and non-spin-polarized (LDFT) calculations were performed with the full potential linearized muffin-tin orbital (FP-LMTO) code developed by J. M. Wills [8]. Additional calculations were done with the plane wave pseudopotential code developed by Lin Yang [3], which is presently limited to LDFT. Troullier-Martins pseudopotentials were used in the plane wave calculations, with a cutoff energy of 70 Ry. The plane wave code is highly efficient numerically and permits the treatment of large cells, up to at least several dozen atoms. The FP-LMTO code achieves high numerical precision in self-consistent solutions to density functional theory, but is not as readily applied to large cells as the plane-wave formulation.

RESULTS

Electronic Spectra

Most Mn oxides undergo transitions to antiferromagnetic states at Neel temperatures that are below room temperature; disordered local moments with short-range antiferromagnetic correlations exist above T_N. Figure 1 shows the densities of electronic states (DOS) calculated with the FP-LMTO method for antiferromagnetic MnO (rocksalt structure), $LiMnO_2$ in the orthorhombic and monoclinic structures, $LiMn_2O_4$ in the (cubic) spinel structure, and delithiated spinel (Mn_2O_4). The calculations employ experimentally determined lattice constants and internal atomic coordinates. A small unit cell (two formula unit) approximant to the experimentally observed antiferromagnetic spin structure [9] was used for orthorhombic $LiMnO_2$. In the case of monoclinic $LiMnO_2$[10], we used the AF3 configuration identified by Singh [4] as energetically favorable. For spinel and delithiated spinel, we arbitrarily assigned two of the four Mn atoms per primitive unit cell as up spins and the other two as down spins. The pyrochlore-structure Mn sublattice of these systems is known to frustrate antiferromagnetic order and to result in large magnetic unit cells for spinel-derived structures [11,12]. The high-temperature cubic atomic structure [13] was adopted for the $LiMn_2O_4$ spinel; the recently measured [12,14] atomic unit cell (tetragonal or orthorhombic) below the Verwey transition (T_v~290 K) is complex.

The zeroes on the abscissa axes in Fig. 1 denote Fermi levels. The lowest-lying states in each of the five systems correspond to the filled oxygen $2p$ bands. The Mn d-bands straddle the Fermi level and are therefore only partially occupied. This band ordering is at variance with Hartree-Fock calculations [15], where the filled Mn-d bands lie below the O-p bands, as a consequence of large spin splitting (~25 eV). The spin splitting of the Mn d-bands calculated within LSDFT is only about 3 eV. Photoemission experiments and configuration-interaction (CI) calculations [16], which show a d-band near the Fermi edge, appear to corroborate the band ordering predicted by LSDFT .

The majority spin t_{2g} band is filled for all the systems represented in Fig. 1. The central issue for the application of these materials to Li batteries is the structural instabilities that develop as the filling of the majority spin e_g band is varied during the lithiation cycle. The majority spin e_g and t_{2g} bands are both filled in rocksalt MnO, in which Mn adopts the maximum magnetic moment 5 μ_B. (This system is included for comparison, but of course has no significance for batteries.) The lithiated manganese dioxide systems, monoclinic and orthorhombic $LiMnO_2$, correspond to a higher Mn oxidation state, 3+, and e_g is therefore only half filled. The Jahn-Teller (JT) distorted Mn-O coordination octahedra in these systems split the occupied and unoccupied e_g bands and result in a gap (a small one in the case of the orthorhombic structure, but we have not employed the full antiferromagnetic unit cell for this system [9]). If $LiMn_2O_4$ spinel is considered to possess an equal mixture of 3+ and 4+ Mn ions, only half of those ions prefer a JT-distorted environment, whereas all Mn environments are equivalent in the assumed cubic structure. It is possible that LSDFT

calculations for the low temperature antiferromagnetic structure [12,14], which are not computationally feasible at present because of its large unit cell, would yield a gap, however, residual disorder of the Mn charge states appears to persist in this system down to the lowest temperatures [12]. In the case of the fully delithiated spinel Mn_2O_4 (λ-MnO_2), the e_g level is completely empty, and a gap is observed between it and the filled t_{2g}.
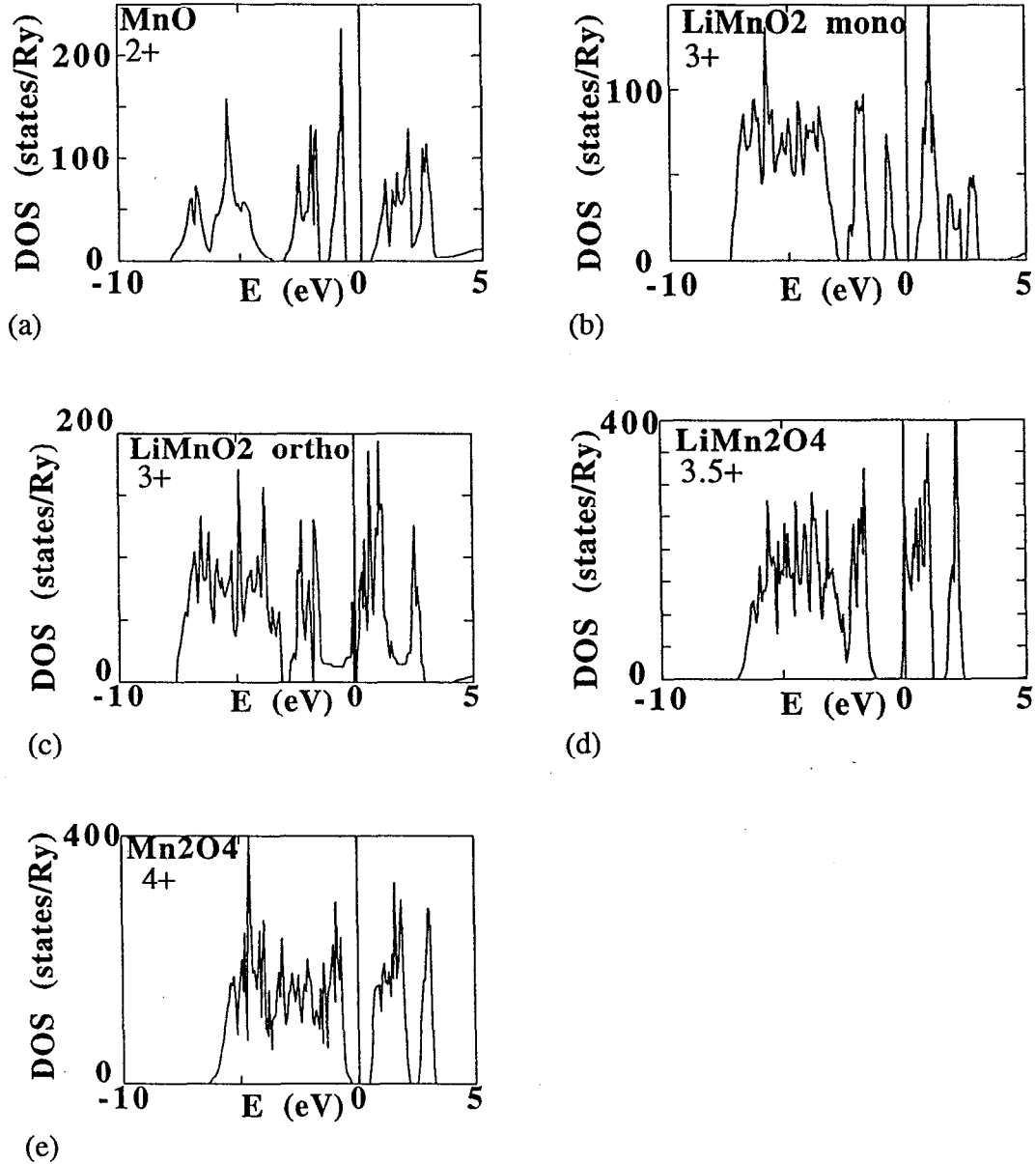

Fig. 1. Densities of electronic states for (a) rocksalt MnO, (b) $LiMnO_2$ in the monoclinic structure, (c) $LiMnO_2$ in the orthorhombic structure, (d) spinel $LiMn_2O_4$, and (e) delithiated spinel Mn_2O_4, calculated with the FP-LMTO method. Antiferromagnetic spin configurations assumed in all cases. See text for discussion.

Despite the energy gaps that appear in Fig. 1, these systems should not be regarded as band insulators. The observed polaronic character of electron transport indicates that electron localization effects that are beyond the scope of LSDFT are significant for Mn oxides. Nevertheless, the work of Mishra and Ceder [5] provides evidence that density functional theory can yield realistic total energies and relative stabilities of competitive Mn-oxide structures.

Jahn-Teller Distortion

Technically, the most difficult regime for first principles calculations is that for which both 3+ and 4+ Mn oxidation states are present, as for example, in $Li_xMn_2O_4$ (0<x<1). In such systems, a disordered arrangement of JT-distorted octahedra typically occurs in conjunction with a frustrated antiferromagnetic spin configuration. In several spinel-based systems, notably those of the Li-Mn-O ternary system, static JT distortions are observed when the mean Mn oxidation state is below about 3.5 [17]. An additional complication is the order-disorder transitions on the Li sublattice, which have been addressed theoretically in the context of Co oxides [1,2], but not Mn oxides. The treatment of all these features simultaneously (i.e, the JT distortions, the antiferromagnetic structure, and the Li configuration at arbitrary x) poses a severe challenge to theory.

The "endpoints" with mean Mn valence very close to either 3 or 4 are relatively more tractable from the standpoint of first principles calculations than the mixed valent regime. In the case of 3+ Mn ions (e.g., in monoclinic [4] and orthorhombic [9] $LiMnO_2$), the JT distortions are uniform throughout the crystal, and the antiferromagnetic structure is unfrustrated, which leads to a relatively small unit cell. In the case of 4+ Mn ions, although the magnetic unit cell may be frustrated (e.g., in λ-MnO_2 [11]), JT distortions are absent, and even non-spin-polarized LDFT calculations may be adequate for some purposes. Thus, we find excellent agreement between calculated internal coordinates and experiment in non-spin-polarized pseudopotential LDFT calculations for α-MnO_2(hollandite), as well as for the electrochemical potential of an inserted Li atom; that work will be presented elsewhere.

Cobalt Doping of Layered $LiMnO_2$

The mixed valent regime is crucial to the operation of Li batteries. A practical difficulty is the limited cycle lifetime of Mn-based systems resulting from JT-induced structural transformations [17]. This shortcoming has motivated the exploration of strategies to suppress the JT distortion. The recent discovery [7] that the rhombohedral (α-$NaFeO_2$) structure of $LiMnO_2$ is stabilized with respect to the (JT distorted) monoclinic form by substitution of only 10% Co suggests that JT-distortion suppression may be possible even at mean Mn valences well below 3.5.

The detailed mechanism for this suppression has yet to be established. Experience with the somewhat analogous JT system perovskite $LaMnO_3$ may be relevant because: (i) only 20% divalent doping (Sr) on the La sublattice suppresses the cooperative JT phase transition [18], and (ii) Co substituted on the Mn sublattice is divalent [19]. These results suggest that modest levels of divalent cobalt in $Li(Co_xMn_{1-x})O_2$ might be sufficient to suppress the JT distortion.

We have begun FP-LMTO calculations on $Li(Co_xMn_{1-x})O_2$ to elucidate the effect of Co doping. Both the monoclinic and the rhombohedral structures were considered, and the AF3[4] antiferromagnetic spin configuration was assumed. The dopant calculations employ one Co atom in a 16-atom cell ($x = 0.25$). Calculations for 8-atom undoped cells ($x = 0.0$) were also performed. For the undoped case, non-spin-polarized and ferromagnetic as well as antiferromagnetic configurations were investigated. These calculations (as well as those presented above for the electronic densities of states) are based on the LSDFT and do not

include the GGA [5,6]. Our calculations have thus far been restricted to the experimental atomic coordinates [10] for the monoclinic structure and the LDFT-predicted [20] atomic coordinates for rhombohedral $LiMnO_2$, and lattice relaxation was not considered either in the doped or the undoped cases.

The total energy difference between the rhombohedral and monoclinic $Li(Co_xMn_{1-x})O_2$ structures in the undoped case, $\Delta e_{r-m}(x=0)$, was found to be 0.18 eV/formula unit, consistent with the known stability of the monoclinic structure [10]. We note, however, that Mishra and Ceder [5] found the ferromagnetic rhombohedral structure to be more stable than the antiferromagnetic monoclinic structure at the LSDFT level, and only at the GGA level was the latter more stable. We expect, however, that valid trends may be discerned by comparing doped and undoped cases at the same level of approximation.

In the case of the doped system, we find $\Delta E_{-m}(x=0.25)$ to be −0.20 eV/formula unit. If we take at face value both this result and that for the undoped system, it would suggest that $\Delta E_{-m}(x \sim 0.1)$ is zero, consistent with the experimental observation of rhombohedral structure stabilization at 10% doping [7]. Analysis of the spin-up and spin-down integrated charge densities in the muffin-tins of the Mn atoms, however, shows them (in both monoclinic and rhombohedral structures) to be unchanged by the Co dopant. This result suggests that no charge transfer takes place, and the oxidation state of Co is 3+ rather than 2+. We suspect, however, that the neglect of lattice relaxation may be giving misleading results. Since the JT environment of monoclinic $LiMnO_2$ is unfavorable for Co, we expect that the coordinated oxygens may relax appreciably, making it favorable for neighboring Mn to reduce the Co oxidation state to 2+. This condition would increase the oxidation state of Mn above 3+. This conjecture, of course, must be confirmed or refuted by explicit calculation, which is now in progress.

CONCLUSION

First principles calculations for lithiated Mn oxides are most difficult in the mixed valent regime, which is the regime of greatest practical interest. A direction that we are currently pursuing is to apply such calculations to gain an understanding of how dopants may suppress the cooperative JT phase transitions that affect the cycle life of Mn-based electrodes in Li batteries.

ACKNOWLEDGMENTS

REFERENCES

1. A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse, and J. Hafner, Phys. Rev. B **58**, 2975 (1998).

2. C. Wolverton and A. Zunger, Phys. Rev. Lett. **81**, 606 (1998).

3. R. Benedek, M. M. Thackeray, and L. H. Yang, Phys. Rev. B **56**, 10708 (1997); Materials Research Society Symposium Proceedings Vol. **496**, 115 (1998).

4. D. J. Singh, Phys. Rev. B **55**, 309 (1997).

5. S. K. Mishra and G. Ceder, Phys. Rev. B, in press.

6. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992)

7. A. R. Armstrong, R. Gitzendanner, A. D. Robertson, and P. G. Bruce, Chem. Commun. **17**, 1833 (1998).

8. J. M. Wills, unpublished.

9. J. E. Greedan, N. P. Raju and I. J. Davidson, J. Solid State Chem. **128**, 209 (1997).

10. R. Armstrong and P. G. Bruce, Nature **381**, 499 (1996); F. Capitaine, P. Gravereau, and C. Delmas, Solid State Ionics **89**, 197 (1996).

11. J. E. Greedan, N. P. Raju, A. S. Wills, C. Morin, J. Britten, H. Dabkowska, and S. M. Shaw, Chem. Mater. **10**, 3058 (1998).

12. A. S. Wills, N. P. Raju, and J. E. Greedan, preprint (1998).

13. A. Yamada and M. Tanaka, Mat. Res. Bull. **30**, 715 (1995).

14. J. Rodriguez-Carvajal, G. Rousse, C. Masquelier, and M. Hervieu, Phys. Rev. Lett., in press (1998).

15. W. C. Mackrodt and E. A. Williamson, Phil. Mag. B **77**, 1077 (1998).

16. R. Lad and V. E. Henrich, Phys. Rev. B **38**, 10860 (1988).

17. M. M. Thackeray, Prog. in Solid State Chem. **25**, 1 (1997).

18. B. A. A. Ellemans, B. van Laar, K. R. van der Veer, and B. O. Loopstra, J. Solid State Chem. **3**, 328 (1971).

19. J.-H. Park, S.-W. Cheong, and C. T. Chen, Phys. Rev. B **55**, 11072 (1997).

20. M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, Phys. Rev. B **56**, 1354 (1997).